

Electrochemical Studies on Ion Pairs Formation of Trimethylsulfonium Halides in 2-Propanol at Different Temperatures

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Abstract-The conductance data of trimethylsulfonium halides (bromide and iodide) in 2-propanol at various temperatures (25, 30, 35 and 40°C) are presented. The results were construed by applying the Fuoss-Onsager equation to determine the characteristic parameters: equivalent conductance at infinite dilution Λ_0 , association constant K_A , the distance of closest approach of ions \bar{a} . A comparison was done between the value of \bar{a}° and the sum of calculated electrostatic Stokes' radii R_+ and R_- , their sum is likened to \bar{a} value. Thermodynamic functions such Gibbs free energy change ΔG_0 , enthalpy change ΔH_0 , change in entropy ΔS_0 and the activation energy (ΔE_s) were estimated.

Keywords- *Trimethylsulfonium Halides, Equivalent Conductance at Infinite Dilution (Λ_0), Ion Association, Activation Energy and Thermodynamic Functions*

I. INTRODUCTION

Electrolytes in the primary alcohols 1,2 and amides 3 appear to exhibit many of the properties previously observed only in water 4,5 and were attributed to the unique structure of that solvent. In alcohols, ionic association was found to increase with anionic size, a result contrary to the predictions of the electrostatic theory. This was interpreted in terms of a multiple-step association process involving hydrogen bonded solvation of anions in the homologous series methanol to 1-propanol. In water and formamide, an analysis of the concentration dependence of conductance shows that the results are consistent with a small amount of ionic association similar to that observed in the normal alcohols and suggests a rather general pattern of behaviour in hydrogen bonding solvents. In order to study this further we have investigated electrolytes in 2 propanol, an alcohol which is expected to show somewhat different hydrogen bonding behaviour.

It has been found recently that the dielectric constant of the medium plays a very important role concerning the behaviour of electrolytes in solution. Various factors may influence the dielectric constant of the medium in the immediate neighborhood of an ion⁶. It was found that in very dilute solutions the dielectric constant of the pure solvent is the proper value to use for so-called "Limiting Law".

Furthermore, it has been shown that changes of the dielectric constant of the medium are closely connected with the corresponding changes of the velocity of homogeneous reaction in solutions. An approach to a theoretical interpretation correlating the changes in medium and the simultaneous changes in the velocity of certain catalyzed reactions was reported⁶.

The effect of solvent may be considered as being twofold:

- Stabilize the pair due to the hydrogen bond chains in the alcohol.
- Solvate anions by hydrogen bond⁷ so that the expected K_A values may increase with anionic radius of salts with the same cation.

The participation of alcohols in the ion-pair formation equilibrium therefore, should involve both steric effect and columbic effect. On the basis of this approach, the structure modifications of the alcoholic polymers are generated by added solvents should result in a variable influence of the alcohol molecules on the ion-pair association of electrolytes.

Several 3-parameters equation^{8,9} and 4-parameters equation¹⁰⁻¹³ were suggested to illustrate the relation between K_A and \bar{a}° and Λ_0 . All of which are based on the model of charged hard spheres in a dielectric continuum.

This paper reports the measurements of the conductance of trimethylsulfonium halides in 2-propanol at different temperatures (25, 30, 35 and 40°C). Fuoss-Onsager three parameters equation is applied for uni-univalent electrolyte (trimethylsulfonium halides) to explicate K_A , the solvent separated ion-pair model² is used.

Ultimately, the thermodynamic functions (ΔH_0 , ΔG_0 , ΔS_0) and energy of activation (ΔE_s) were calculated and interpreted according to interaction of solvent at different temperatures.

Fuoss and Onsager⁸, utilized the sphere in continuum model and the next equation was formulated:

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + (J - B\Lambda_0)C\gamma - K_A C\gamma \Lambda f^2 \quad (1)$$

Where, Λ is the equivalent conductance ohm-1equiv-1cm², equivalent conductance at infinite dilution (Λ_0), C is the

concentration (equiv/l) and ion association constant (KA), is the degree of dissociation which is determined by the equation:

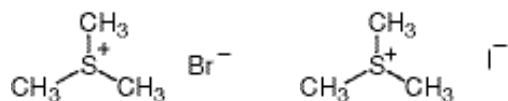
$$\gamma = \Lambda / \Lambda_0 - S(C\Lambda / \Lambda_0)^{1/2} \quad (2)$$

S and E are theoretically predicted constants, which depend on the dielectric constant of the medium, absolute temperature and the viscosity (D, T and η respectively).

The aim of the present work is to study and understand the mobility and association process of the compound "trimethylsulfonium halides" by measuring its conductance in 2-propanol at various temperatures (25, 30, 35 and 40°C) followed by determining the thermodynamic functions (ΔG_0 , ΔH_0 , ΔS_0 and ΔE_s) to describe how the system responds to changes in its environment and get information about trimethylsulfonium halides behaviour in the solvent system studied (2-propanol).

II. EXPERIMENTAL

All salts were highly purified reagent grade and used without further purification. Where trimethylsulfonium bromide (Me₃S.Br) and trimethylsulfonium iodide (Me₃S.I) are Analar analytical reagent "BDH". 2-propanol (B.D.H, Analar grade) was used without any further purification.



The specific conductance κ° for 2-propanol at different temperatures (25, 30, 35 and 40°C) was found to be (1.1- 2.6 x 10⁻⁷) ohm⁻¹cm⁻¹.

All solutions were prepared by weight. Salts were weighed on a microbalance which reads to ± 0.1 mg. Dilution was carried out successively into the cell by siphoning the solvent by means of weighing pipette. Conductivity Bridge was model Crison GLP31+ and the cell with bright platinum electrodes was used. The cell constant was 0.1 cm⁻¹ for dilute solutions. The solvent constants used in all calculations were taken as reported 14-17, i.e., densities (d_{25}°) = 0.78110 g cm⁻³, (d_{30}°) = 0.77712 g cm⁻³, (d_{35}°) = 0.77288 g cm⁻³, (d_{40}°) = 0.76879 g cm⁻³, respectively, the viscosities (η_{25}°) = 2.070 x 10⁻² P, (η_{30}°) = 1.783 x 10⁻² P and (η_{35}°) = 1.546 x 10⁻² P, (η_{40}°) = 1.374 x 10⁻² P, respectively and the dielectric constants (D_{25}°) = 19.40, (D_{30}°) = 18.69, (D_{35}°) = 17.89, (D_{40}°) = 17.07, respectively.

III. RESULTS AND DISCUSSION

A. Conductance of trimethylsulfonium halides (bromide and iodide) in 2-propanol at several temperatures

The measured equivalent conductance data are shown in Tables (1-2). By plotting the extrapolation of Λ against $C^{1/2}$, an approximate value of Λ_0 was obtained. More precise values of Λ_0 were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{(C\Lambda S(z)f^2)}{K_D \Lambda_0^2} \quad (3)$$

Where KD is the dissociation constant and S (z) is a function of z called Shedlovsky' s function that was tabulated by Daggett. The z value could be determined from the expression:

$$Z = a(C\Lambda)^{1/2} / \Lambda_0^{3/2} \quad (4)$$

Where α is the limiting tangent (Onsager slope). The plot of $1/\Lambda S(z)$ versus $(C\Lambda S(z)f^2)$ gives $1/\Lambda_0$ as the intercept and $1/K_D\Lambda_0^2$ as the slope. More accurate values of Λ_0 , J(a), a° and KA were obtained from Fuoss-Onsager equation. The starting Λ_0 value was resulted from Fuoss-Kraus-Shedlovsky equation by the assist of specific computer program that was programmed on an IBM-PC. The desired accuracies in these calculations are ± 0.02 for Λ_0 ; ± 2 for (J less than 200), ± 5 for (J with values range from 200 to 1000) and ± 10 for (J more than 1000).

The standard deviation $\sigma\Lambda$ was calculated using the equation 18:

$$\sigma_A = \frac{\{\sum(\Lambda_{\text{calculated}} - \Lambda_{\text{observed}})^2\}^{1/2}}{(N-3)^{1/2}} \quad (5)$$

where N is the number of experimental points.

Figures (1-2) displays the variation of J with a° for trimethylsulfonium halides (bromide and iodide) in 2-propanol at 25, 30, 35 and 40°C. Through the knowledge of the average value of J, The average value of a° could be calculated by interpolation. This J value was obtained from the computer reading, where J is being a function of a° and has the following equation 8:

$$J = \sigma_1 \Lambda^\circ + \sigma_2 \quad (6)$$

Where σ_1 and σ_2 are the functions of J. The derived constants are represented in Tables (3-4) and it is observed that Λ_0 , KA, a_0 for trimethylsulfonium bromide and trimethylsulfonium iodide increase with increasing the temperatures in 2-propanol.

The values of Λ_0 increase with increasing the size of the anion, in the order { Λ_0 trimethylsulfonium iodide > Λ_0 trimethylsulfonium bromide}, according to ionic equivalent conductance of anions.

KA increases with decreasing the dielectric constant of the medium and increase with increasing the temperatures for the two salts; this was explained on the basis that, ionic mobility decrease as the dielectric constant of the medium decrease and hence the chance to form ion-pairs increases.

The values of KA increases with increasing the size of the anion, in the order {KA trimethylsulfonium iodide > KA trimethylsulfonium bromide}, according to the electrostatic theory.

The trend of KA in the present work was explained in the light of the U term as represented in the following equation 19:

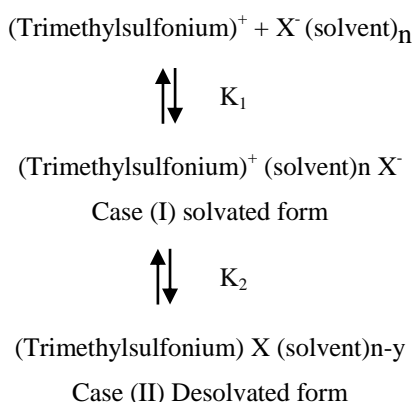
$$\ln KA = \ln(4\pi N a^3 / 3000) + (e^2 / a^\circ D k T) + U \quad (7)$$

where,

$$U = \Delta S/k - E_s/Kt \quad (8)$$

$\Delta S/k$ is the entropy Boltzman constant ratio which illustrates the probability of the orientation of solvent molecules around the free ions, and E_s/kT is an energy relationship which includes the energy of the solvent molecules with respect to both free ions (i.e. ion-dipole interaction) and ion-pairs. In case of 2-propanol in Tables (5-6), the U term increases with increasing the temperatures for the two salts, i.e. the entropy term is more predominant than the ion-dipole term for the two salts.

Finally, the solvent separated ion-pair model can be applied 2. In this model a multiple-step association was suggested, i.e. solvent separated and contact ion-pair can be illustrated in the following scheme:



Where y = number of escaping solvent molecules from solvation.

Thus, the association constant is given by the following expression:

$$K_A = K \frac{[C_{(\text{ion-pairs})}]}{\Sigma [C_{(\text{Trimethylsulfonium})^+}] [C_{X^- (\text{Solvent})_n}]} = K_1 (1 + K_2) \quad (9)$$

where $K_A = K \Sigma$ is obtained from the conductance measurements and since $K_1 = 4 \pi N a_0^3 \epsilon b / 3000$ then K_2 can be calculated and $b = e^2 / a_0 D T k$

In case of trimethylsulfonium bromide and iodide in 2-propanol at different temperatures, the results compiled in Tables (5-6) indicated that K_2 increases with increasing the temperature, i.e. Ion-pair preferred the desolvated form (case II) than the solvated form (case I).

1) Radii of ions

The electrostatic radii R^+ and R^- are given by Stokes' equation:

$$R^\pm = 0.8194 \times 10^{-8} / \lambda_0^\pm \eta_0 \quad (10)$$

where η_0 is the viscosity of pure solvent and λ_0^\pm is obtained from the intercept of the straight line, resulting from the plots of Walden product $\Lambda_0 \eta_0$ versus the reciprocal of the molecular weight as previously discussed²⁰.

From the data in Tables (7-8), it could be noticed that; in case of 2-propanol at 25, 30, 35 and 40°C, the values of Λ_0 were greater than electrostatic radii ($R^+ + R^-$) obtained from stokes equation. This was due to the solvation of ions.

B. Thermodynamic functions measurements of trimethylsulfonium halides (bromide and iodide) in 2-propanol:

It is evident from Tables (9-10) that the values of Λ_0 increase regularly with increase in temperature for trimethylsulfonium bromide and iodide, indicating higher mobility of the ions in all solvent systems studied. This is due to the fact that the increase in thermal energy results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules lead to higher frequency and higher mobility of ions²¹. Also, it is clear that the association constant (K_A) values increase with increase in temperature and with increase in alcohol content and also with the increase of the $-CH_2-$ group in alcohol [22].

Since the conductance measurements of an ion depend on its mobility, it is quite reasonable to treat the conductance data similar to the one that employed for the processes taking place with change of temperature [23], i.e.

$$\Lambda_0 = A e^{-\Delta E_s / RT}$$

OR (11)

$$\log \Lambda_0 = \log A - (\Delta E_s / 2.303RT),$$

where A is the frequency factor, R is the ideal gas constant and ΔE_s is the Arrhenius activation energy of transport processes.

The values of ΔE_s have been computed from the slope ($-\Delta E_s / 2.303RT$) of the plot of $\log \Lambda_0$ vs. $1/T$ and recorded in Tables (9-10) and Figures (3,4). From the tables, the activation energy ΔE_s is positive value for the two salts in all solvents. Their values increased from bromide to iodide, indicate the higher mobility of the ions in solution and hence higher Λ_0 values.

The free energy change ΔG^0 for the association process is calculated [23],

$$\Delta G^0 = -RT \ln K_A, \quad (12)$$

It is evident From Tables (9-10), that the free energy change (ΔG^0) values are negative for the two salts (Br^- and I^-) in all solvent systems studied. This means that the association process is favored over the dissociation process in all solvent systems.

According to the results of the calculated thermodynamic parameters as shown by Tables (9-10) and Figures (5-6), the standard enthalpy changes, (ΔH^0), can be obtained from the slope ($-\Delta H^0 / 2.303R$) of the plot of $\log K_A$ against $1/T$ by using the Van't Hoff's isochore equation

$$d \ln K_A / dT = \Delta H^0 / RT^2 \quad (13)$$

Then,

$$2.303 \log K_A = -(\Delta H^\circ / R)(1/T) + \Delta S^\circ / R \quad (14)$$

or

$$2.303R \log K_A = \left(\Delta S^\circ - \frac{\Delta H^\circ}{T} \right) \quad (15)$$

The positive values of (ΔH°) for the two salts (Br^- and I^-) show that the association processes are endothermic in nature and the calculated entropy change (ΔS°) , from Gibbs equation;

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (16)$$

The positive values of (ΔS°) for two salts (Br^- and I^-) indicates the randomness of ions in all solvent systems studied.

The values of ΔH° , ΔG° , ΔS° are recorded in Tables (9-10) for trimethylsulfonium bromide and iodide in 2-propanol at different temperatures (25, 30, 35 and 40°C). (ΔG°) values decrease with increase in temperature. The decrease in (ΔG°) values for the (two salts) to more negative values at increasing temperature favors the transfer of the released solvent molecules into bulk solvent and leads to a smaller (ΔG°) values. It was observed that (ΔH°) values increase in the order: $\text{I}^- > \text{Br}^-$. The (ΔH°) values were found to be positive in all alcohols. Positive and high (ΔH°) values can be attributed to the interaction between ions [24]. As presented in Tables (9-10) (ΔS°) values were positive because of decrease in the solvation of ion-pair compared to that of the free ion [25-27]. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules.

The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of ions, (ii) charge density on ions, (iii) electrostriction of the solvent molecules around the ions and (iv) the penetration of the solvent molecules inside the space of ions [28].

Bag, et al. [29], have measured the conductance of Co (III) salt monochloride in MeOH-H₂O mixtures at different temperatures (25, 30, 35 and 40 °C). It was found that, at a particular temperature ΔG° becomes more negative with increase in temperature. This indicates that ion-pair association is favored with lowering of dielectric constant of medium. A positive entropy change is explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderness [30].

Dash, et al. [21], have measured the conductance of Co (III) salt of chloride and bromide in different composition of H₂O-MeOH, H₂O-EtOH and H₂O-n-PrOH at different temperatures. It was found that, the association constant K_A values of Co (III) salts of chloride and bromide increase with increase in

temperature. It is evident that the activation energy E_s is positive for both K_A in all solvents and free energy change ΔG° values are negative for both association constants in solvent with increase the temperature. This indicates that the association process is favored over dissociation process in all solvent systems. The positive values of ΔH° for both salts show that the association processes are endothermic in nature. The positive value of ΔS° indicates the randomness of ions in solvent system studied [21].

S.Pura [24], has measured the conductance of ferric chloride (FeCl_3) in primary alcohols at different temperatures. It was found that, at particular temperature ΔG° values decrease with increase in temperature. The decrease in ΔG° values for FeCl_3 to more negative values at increasing temperature favor the transfer of the released solvent molecules into the bulk solvent and lead to a smaller ΔG° values. The experimental values of ΔG° for FeCl_3 varied in the order: $\text{MeOH} > \text{EtOH} > 1\text{-PrOH} > 1\text{-BuOH}$. At the temperature range studied, It was observed that the ΔH° values of FeCl_3 in alcoholic organic solvents decrease in the order of $\text{MeOH} > \text{EtOH} > n\text{-PrOH} > n\text{-BuOH}$. The values of ΔH° were found to be positive in all alcohols. Positive and high ΔH° can be attributed to the interaction between ions. The ΔS° values of FeCl_3 in primary alcohols were found to decrease in the order $\text{MeOH} < \text{EtOH} < n\text{-PrOH} < n\text{-BuOH}$, indicating a weakening in the ion solvation due to the formation of ion pairs. The values of ΔS° for all alcohols used in the study were positive because of the decrease in solvation of the ion pairs compared to that of the free ions. The positive ΔS° values for FeCl_3 in all alcohols may be attributed to the increase in the degree of freedom upon association mainly due to the release of solvent molecules. In other words, the solvation of ions became weaker as soon as the ion pair formation occurs. The radii of solvent molecules and the degree of solvation decreases with of the length of hydrocarbon ($-\text{CH}_2-$) groups of primary alcohols. For that reason, higher increase in entropy was observed, and the changes of entropy became more positive values from MeOH to n- BuOH. Positive values of ΔH° and ΔS° values for FeCl_3 can be attributed to the counter balance entropy change resulting from both short- and long- term desolvation of ions. Positive (ΔS°) values attributed to desolvation of ions are also supported by the positive enthalpy values indicating a lack of the covalent bonds [24].

El-Hammamy et al. [31], have measured the conductance of cobalt (III) salt, chloropentammine chloride, in water at different temperatures 40 → 60°C. The results were analyzed using Fuoss-Edelson equation [32], from which the values of Λ_0 and K_A were obtained for the salt at different temperatures. It was found that, Λ_0 and K_A increase with increasing the temperature. Thus, from the plot of $\log \Lambda_0$ versus $1/T$ for the salt of cobalt (III) in water at different temperatures, the positive value of ΔE_s has been evaluated, and also ΔH° , ΔG° , ΔS° for the salt. It was found that, ΔH° and ΔS° are positive at a particular temperature but ΔG° is negative, this may be due to the increase in association of ions and thus solvation process was less. Endothermic solvation needs energy to break the bonds around free ion and ion-pairs, i.e., endothermic solvation process and ΔS° is constant but ΔG° decreases in the negative value with increasing the temperature.

El-Hammamy et al. [33], have measured the conductance of 1:1 s-acetylthiocholine salts (Cl⁻, Br⁻, I⁻ and ClO₄⁻) in water at different temperatures (25,30,35oC). The results were analyzed using Fuoss-Onsager equation 8, from which the values of Λ_0 , K_A and a° (solvation) were obtained. It was found that, Λ_0 and a° increase with increasing the temperature while K_A decreases with increasing the temperature, for all salts of s-acetylthiocholine, according to electrostatic attraction theory. The limiting equivalent conductance and dissociation degree were also increased as the temperature increased, indicating higher solvation process [33]. The negative values of different thermodynamic parameters ΔH° , ΔG° , ΔS° , for all salts studied in the used solvent, indicated that exothermic association process was less energy-consuming and more stabilized [34].

El-Hammamy et al. [35], have measured the conductance of 1:1 s-acetylthiocholine salts (Br⁻, I⁻ and ClO₄⁻) in acetonitrile at different temperatures (25, 30, 35 and 40°C). The results were analyzed using Fuoss-Onsager equation ⁸, from which the values of Λ_0 , K_A and a (solvation) were obtained. It was found that, Λ_0 and K_A increase with increasing the temperature. Thus, from the plot of $\log \Lambda_0$ versus $1/T$ for acetylthiocholine halides and perchlorate in acetonitrile solutions at different temperatures, positive values of ΔE_s have been evaluated, also ΔH° , ΔG° and ΔS° for all salts. It was found that, ΔH° and ΔS° have positive values at a particular temperatures but ΔG° has negative value. This is due to lower solvation processes but association of ion increase with thermodynamic parameters. Endothermic solvation process needs energy to break the bond around free ion and ion-pairs, i.e. this process was less energy-consuming and more stabilized.

El-Hammamy et al. [36], have measured the conductance of sodium diethyldithiocarbamate in methanol at different temperatures (25, 30, 35 and 40°C). The results were also analyzed using Fuoss-Onsager equation ⁸, to determine the characteristic parameters: equivalent conductance at infinite dilution Λ_0 , association constant K_A , the distance of closest approach of ions \AA . After calculation of the electrostatic Stokes' radii (R^+ and R^-), their sum is likened to \AA value. Thermodynamic functions such Gibbs free energy change ΔG° , enthalpy change ΔH° , change in entropy ΔS° and the activation energy (ΔE_s) were estimated.

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TABLE I. CONDUCTANCE OF TRIMETHYLSULFONIUM BROMIDE IN 2-PROPANOL AT DIFFERENT TEMPERATURES:

Trimethylsulfonium Bromide at 25°C			
104C	C1/2	106 μ S	Λ
2.5524	0.0160	6.36	24.9169
2.2830	0.0151	5.73	25.0975
2.0793	0.0144	5.25	25.2488
1.9064	0.0138	4.84	25.3869
1.7632	0.0133	4.50	25.5208
1.6276	0.0128	4.17	25.6198
1.5055	0.0123	3.88	25.7711
1.4083	0.0119	3.64	25.8452
Trimethylsulfonium Bromide at 30°C			
1.6306	0.0128	5.63	34.5270
1.4652	0.0121	5.15	35.1466
1.3354	0.0116	4.76	35.6821
1.2260	0.0111	4.43	36.1325
1.1313	0.0106	4.14	36.5952
1.0492	0.0102	3.88	36.9777
0.9801	0.0099	3.66	37.3412
0.9215	0.0096	3.47	37.6558
Trimethylsulfonium Bromide at 35°C			
2.0791	0.0144	7.51	36.1208
1.8700	0.0137	6.92	37.0054
1.7136	0.0131	6.47	37.7547
1.5744	0.0125	6.05	38.4266
1.4581	0.0121	5.69	39.0231
1.3559	0.0116	5.37	39.6035
1.2659	0.0113	5.07	40.0481
1.1906	0.0109	4.81	40.3998
Trimethylsulfonium Bromide at 40°C			
2.7555	0.0166	11.26	40.8632
2.4753	0.0157	10.38	41.9339
2.2603	0.0150	9.64	42.6474
2.0708	0.0144	8.99	43.4120
1.9215	0.0139	8.49	44.1832
1.7770	0.0133	7.95	44.7361
1.6620	0.0129	7.52	45.2457
1.5636	0.0125	7.15	45.7261

* equiv L⁻¹
** ohm⁻¹ equiv⁻¹ cm²

TABLE II. CONDUCTANCE OF TRIMETHYLSULFONIUM IODIDE IN 2-PROPANOL AT DIFFERENT TEMPERATURES:

Trimethylsulfonium Iodide at 25°C			
104C	C1/2	106 μ S	Λ
2.9955	0.0173	6.92	23.1011
2.6624	0.0163	6.28	23.5877
2.4163	0.0155	5.79	23.9620
2.1969	0.0148	5.34	24.3063
2.0191	0.0142	4.97	24.6147
1.8629	0.0136	4.64	24.9074
1.7320	0.0132	4.35	25.1144
1.6173	0.0127	4.10	25.3508
Trimethylsulfonium Iodide at 30°C			
1.3010	0.0114	5.22	40.1225
1.1604	0.0108	4.72	40.6734
1.0492	0.0102	4.32	41.1741
0.9527	0.0098	3.96	41.5657
0.8781	0.0094	3.68	41.9071
0.8142	0.0090	3.44	42.2454
0.7553	0.0087	3.21	42.4987
0.7022	0.0084	3.01	42.8607
Trimethylsulfonium Iodide at 35°C			
0.7509	0.0087	3.23	43.0130
0.6759	0.0082	2.96	43.7876
0.6120	0.0078	2.73	44.6036
0.5623	0.0075	2.54	45.1714
0.5195	0.0072	2.38	45.8055
0.4831	0.0070	2.24	46.3589
0.4507	0.0067	2.11	46.8092
0.4255	0.0065	2.01	47.2300
Trimethylsulfonium Iodide at 40°C			
0.2754	0.0052	1.27	46.1095
0.2505	0.0050	1.18	47.0913
0.2306	0.0048	1.11	48.1242
0.2122	0.0046	1.04	49.0095
0.1972	0.0044	0.98	49.6845
0.1850	0.0043	0.93	50.2599
0.1743	0.0042	0.89	51.0565
0.1627	0.0040	0.84	51.6094

* equiv L⁻¹
** ohm⁻¹ equiv⁻¹ cm²

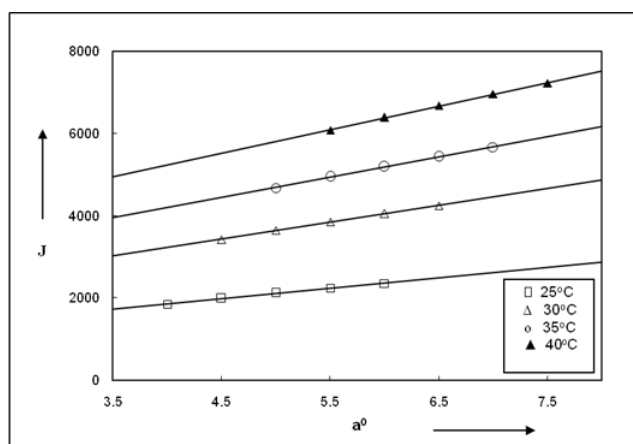


Figure 1. Variation of J and a° of Trimethylsulfonium bromide in 2-propanol at different temperatures

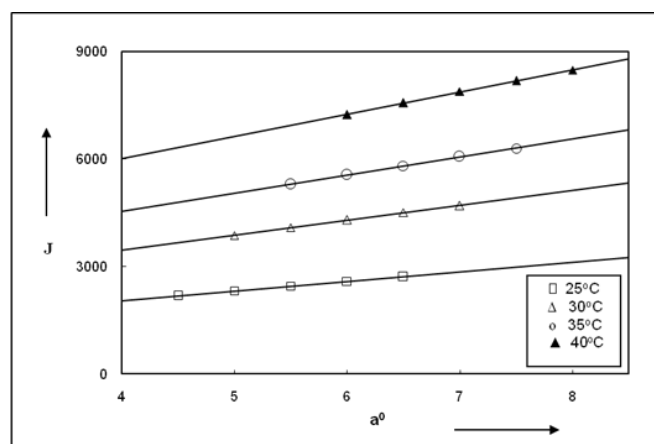


Figure 2. Variation of J and a° of Trimethylsulfonium iodide in 2-propanol at different temperatures.

TABLE III. THE CHARACTERISTIC PARAMETERS TRIMETHYLSULFONIUM BROMIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C DERIVED FROM FUOSS-ONSAGER EQUATION:

Temperature	Λ_{∞} (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K _A	a ^o (Å)	σ_{Λ}
25°C	27.992 ± 0.1500	2118.4	422.35	5.0	0.0177
30°C	45.328 ± 0.1531	3853.2	456.33	5.5	0.0169
35°C	53.676 ± 0.3067	5191.3	513.95	6.0	0.0816
40°C	60.415 ± 0.4424	6680.0	526.42	6.5	0.0849

TABLE IV. THE CHARACTERISTIC PARAMETERS FOR TRIMETHYLSULFONIUM IODIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C DERIVED FROM FUOSS-ONSAGER EQUATION:

Temperature	Λ_{∞} (ohm ⁻¹ equiv ⁻¹ cm ²)	J	K _A	a ^o (Å)	σ_{Λ}
25°C	30.657 ± 0.1739	2456.7	431.99	5.5	0.0190
30°C	48.141 ± 0.1542	4291.1	462.19	6.0	0.0357
35°C	57.564 ± 0.1501	5818.8	537.21	6.5	0.0466
40°C	68.614 ± 0.3273	7876.2	542.89	7.0	0.1072

TABLE VII. CALCULATIONS OF THE RADII OF THE IONS FOR TRIMETHYLSULFONIUM BROMIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C:

Temperature	⁽¹⁾ Λ_{∞}	$\lambda_{\infty}^{-} \eta_{\infty}^{-}$ ⁽²⁾	$\lambda_{\infty}^{+} \eta_{\infty}^{+}$ ⁽²⁾	λ_{∞}^{-} ⁽¹⁾	λ_{∞}^{+} ⁽¹⁾	Av. λ_{∞}^{+}	R ⁺ (A ^o)	R ⁻ (A ^o)	R ⁺ +R ⁻	a ^o (A ^o)
25°C	27.992	0.2370	0.3545	11.45	16.542	17.1295	2.3108	3.4571	5.7680	5.0
30°C	45.328	0.2230	0.5939	12.51	32.818	33.3095	1.3796	3.6735	5.0532	5.5
35°C	53.676	0.2114	0.6313	13.68	39.996	40.8350	1.2979	3.8743	5.1723	6.0
40°C	60.415	0.2054	0.6628	14.95	45.465	48.2395	1.2362	3.9890	5.2252	6.5

(1) ohm⁻¹equiv⁻¹cm²
(2) ohm⁻¹equiv⁻¹cm² p

TABLE VIII. CALCULATIONS OF THE RADII OF THE IONS FOR TRIMETHYLSULFONIUM IODIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C:

Temperature	⁽¹⁾ Λ_{∞}	$\lambda_{\infty}^{-} \eta_{\infty}^{-}$ ⁽²⁾	$\lambda_{\infty}^{+} \eta_{\infty}^{+}$ ⁽²⁾	λ_{∞}^{-} ⁽¹⁾	λ_{∞}^{+} ⁽¹⁾	Av. λ_{∞}^{+}	R ⁺ (A ^o)	R ⁻ (A ^o)	R ⁺ +R ⁻	a ^o (A ^o)
25°C	30.657	0.2678	0.3545	12.94	17.717	17.1295	2.3108	3.0590	5.3699	5.5
30°C	48.141	0.2556	0.5939	14.34	33.801	33.3095	1.3796	3.2047	4.5844	6.0
35°C	57.564	0.2456	0.6313	15.89	41.674	40.8350	1.2979	3.3355	4.6334	6.5
40°C	68.614	0.2418	0.6628	17.60	51.014	48.2395	1.2362	3.3884	4.6246	7.0

(1) ohm⁻¹equiv⁻¹cm²
(2) ohm⁻¹equiv⁻¹cm² p

TABLE IX. THERMODYNAMIC PARAMETERS OF TRIMETHYLSULFONIUM BROMIDE IN 2-PROPANOL AT DIFFERENT TEMPERATURES:

T (K)	Λ_{∞} (ohm ⁻¹ equiv ⁻¹ cm ²)	K _A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
298	27.992	422.35	38.60	12.12	-14.98	90.94
303	45.328	456.33			-15.43	90.91
308	53.676	513.95			-15.99	91.25
313	60.415	526.42			-16.31	90.82

TABLE X. THERMODYNAMIC PARAMETERS OF TRIMETHYLSULFONIUM IODIDE IN 2-PROPANOL AT DIFFERENT TEMPERATURES:

T (K)	Λ_{∞} (ohm ⁻¹ equiv ⁻¹ cm ²)	K _A	ΔE_s° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
298	30.657	431.99	40.38	12.99	-15.04	94.06
303	48.141	462.19			-15.46	93.91
308	57.564	537.21			-16.10	94.46
313	68.614	542.89			-16.39	93.87

TABLE V. CALCULATED VALUES OF K₂ AND U FOR TRIMETHYLSULFONIUM BROMIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C:

Temperature	K _A	K ₁	K ₂	U
25°C	422.35	101.5759	3.1579	1.4250
30°C	456.33	89.2275	4.1142	1.6320
35°C	513.95	84.9382	5.0508	1.8002
40°C	526.42	84.7306	5.2128	1.8266

TABLE VI. CALCULATED VALUES OF K₂ AND U FOR TRIMETHYLSULFONIUM IODIDE IN 2-PROPANOL AT 25, 30, 35 AND 40°C:

Temperature	K _A	K ₁	K ₂	U
25°C	431.99	79.9707	4.4018	1.6867
30°C	462.19	74.1086	5.2366	1.8304
35°C	537.21	73.2290	6.3360	1.9927
40°C	542.89	75.0694	6.2318	1.9784

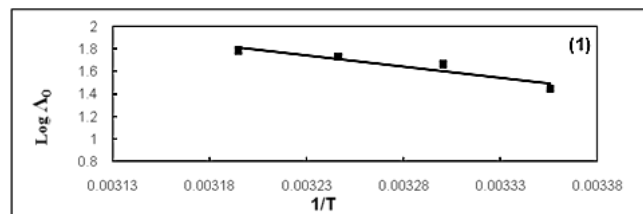


Figure 3. The variation of log Λ_0 vs. 1/T for Trimethylsulfonium bromide in 2-propanol at different temperatures.

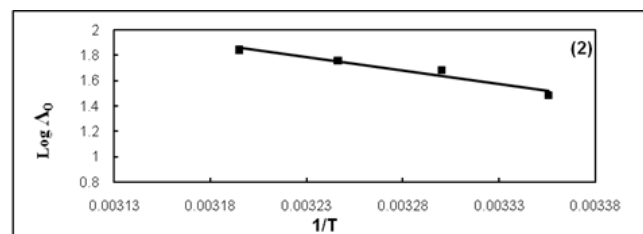


Figure 4. The variation of log Λ_0 vs. 1/T for Trimethylsulfonium iodide in 2-propanol at different temperatures.

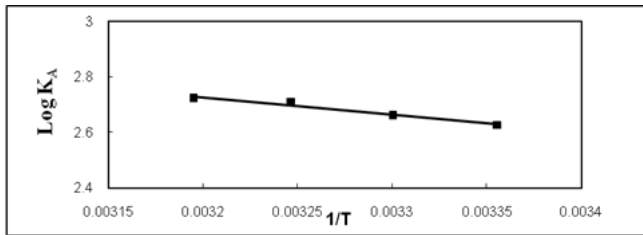
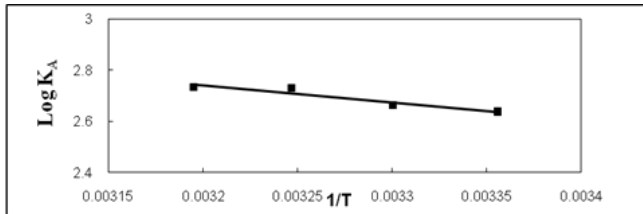


Figure 5. The variation of log K_A vs. 1/T for Trimethylsulfonium bromide in 2-propanol at different temperatures.



The variation of log K_A vs. 1/T for Trimethylsulfonium iodide in 2-propanol at different temperatures.

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